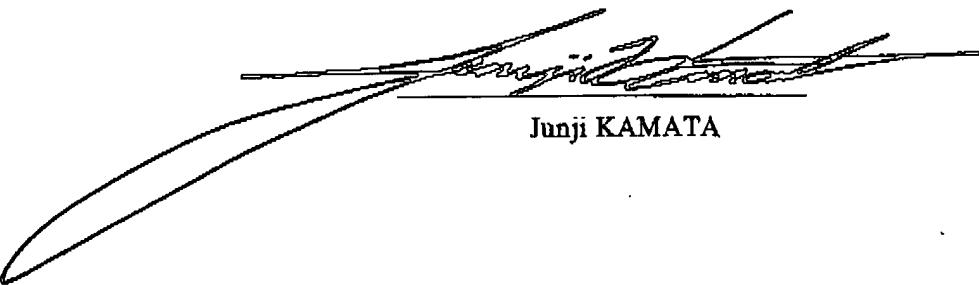


DECLARATION

I, Junji Kamata, Patent Attorney, of SIKs & Co., 8th Floor, Kyobashi-Nisshoku Bldg., 8-7, Kyobashi 1-chome, Chuo-ku, Tokyo 104-0031 JAPAN hereby declare that I am the translator of the certified official copy of the documents in respect of an application for a patent filed in Japan on August 3, 2000 under Patent Application No. 236044/2000 and that the following is a true and correct translation to the best of my knowledge and belief.

Dated: April 3, 2003



Junji KAMATA

PATENT OFFICE

JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s) : FUJI PHOTO FILM CO., LTD.

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Kozo OIKAWA

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【Document name】 Specification

【Title of the invention】 Method for preparing grains of silver salt of organic acid and thermally processed image recording material

【Claims】

【Claim 1】 A method for preparing an aqueous dispersion of grains of silver salt of an organic acid that is obtained by dispersing the silver salt grains of the organic acid into an aqueous solvent; which comprises the steps of reacting (1) a solution containing silver ion in water or in a mixture of organic solvent and water with (2) a solution or suspension containing an alkali metal salt of the organic acid in water or in a mixture of an organic solvent and water, or in an organic solvent, to obtain a silver salt of the organic acid, and conducting dispersion with a high pressure homogenizer or high speed rotary homomixer in the presence of a dispersing agent, and removing by-product salts by ultrafiltration.

【Claim 2】 A method for preparing an aqueous dispersion of grains of silver salt of an organic acid that is obtained by dispersing the grains of silver salt of the organic acid into an aqueous solvent; which comprises the steps of reacting (1) a solution containing silver ion in water or in a mixture of organic solvent and water with (2) a solution or suspension containing an alkali metal salt of the organic acid in water or in a mixture of an organic solvent and water, or in an organic solvent, to obtain a silver salt of the organic acid, and conducting dispersion with a high pressure homogenizer or high speed rotary homomixer in the presence of a dispersing agent with by-product salts being removed by ultrafiltration.

【Claim 3】 The method for preparing an aqueous dispersion of grains of silver salt of an organic acid according to Claim 1 or 2, wherein the dispersing agent has a molecular weight of 3000 or less and is an anionic surfactant having 8–40 carbon atoms.

【Claim 4】 The method for preparing an aqueous dispersion of grains of silver salt of an organic acid according to any one of Claims 1–3, wherein the dispersing agent is used at a concentration of 1–30 weight % of dispersing agent.

【Claim 5】 The method for preparing an aqueous dispersion of grains of silver salt of an organic acid according to any one of Claims 1–4, wherein concentration of the grains of silver salt of the organic acid is 1–10 weight % immediately after the reaction.

【Claim 6】 The method for preparing an aqueous dispersion of grains of silver salt of an organic acid according to any one of Claims 1–5, wherein, after the by-product salts are removed by the ultrafiltration, concentration operation is performed by the ultrafiltration.

【Claim 7】 The method for preparing an aqueous dispersion of grains of silver salt of an organic acid according to any one of Claims 1–5, wherein, after electric conductivity reached within the range of from 20 μ S/cm to less than 300 μ S/cm as a result of the removal of the by-product salts by the ultrafiltration, the dispersion is concentrated to a concentration of 10–70 weight % by the ultrafiltration.

【Claim 8】 A method for producing a thermally processed image recording material comprising a silver salt of an organic acid, a reducing agent for silver ions and a binder on at least one surface of a support, which comprises a step of applying a coating solution for image-forming layer containing an aqueous dispersion of grains of silver salt of an organic acid prepared by the method according to any one of Claims 1–7.

【Claim 9】 A method for producing a thermally processed image recording material comprising a silver salt of an organic acid, a reducing agent for silver ions and a binder on at least one surface of a support, which comprises a step of applying a coating solution for image-forming layer containing an aqueous dispersion of grains of silver salt of an organic acid prepared by the preparation method

according to Claim 8

【Claim 10】 A thermally processed image recording material which is prepared by the method according to claim 8 or claim 9.

【Detailed description of the invention】

【0001】

【Filed of the invention】

The present invention relates to a method for preparing an aqueous dispersion of grains of silver salt of an organic acid which can be used in a thermally processed image recording materials, especially photothermographic material. The present invention also relates to a thermally processed image recording material that utilizes the aqueous dispersion of grains of silver salt of the organic acid, and a method for producing the material.

【0002】

【Relevant art】

In recent years, reduction of amount of waste processing solutions is strongly desired in the field of medical diagnosis from the standpoints of environmental protection and space savings. Therefore, techniques relating to photothermographic materials for use in photographic art processes and medical diagnosis are required which enables efficient exposure by a laser image setter or laser imager and formation of a clear black image having high resolution and sharpness. Such photothermographic materials can provide users with a simple and non-polluting heat development processing system that eliminates the use of solution-type processing chemicals.

【0003】

Methods for forming an image by heat development are described in, for example, U.S. Patent Nos. 3,152,904 and 3,457,075 and D. Klosterboer, "Thermally Processed Silver Systems", Imaging Processes and Materials, Neblette, 8th ed., compiled by J. Sturge, V. Walworth and A. Shepp, Chapter 9, p.279, (1989).

【0004】

Such a photothermographic material contains a reducible non-photosensitive silver salt (e.g., organic acid silver salt), a photocatalyst (e.g., silver halide) in a catalytically active amount and a reducing agent for silver, which are usually dispersed in an organic binder matrix. The photothermographic material is stable at normal temperature, and when the material is heated at a high temperature (e.g., 80°C or higher) after light exposure, black silver images are produced through an oxidation-reduction reaction between the silver halide or reducible silver salt (which functions as an oxidizing agent) and the reducing agent. The oxidation-reduction reaction is accelerated by catalytic action of a latent image of the silver halide generated upon exposure. The silver produced by the reaction of the reducible silver salt in exposed areas provides a black image in contrast to non-exposed areas whereby image can be formed.

【0005】

The silver source used in these systems is generally a silver salt of an organic acid, and various methods for producing it have been known. For example, there can be mentioned the method of preparing a silver salt of an organic acid under coexistence of water and a hardly water-soluble solvent as disclosed in Japanese Patent Laid-open Publication (Kokai, hereinafter referred to as JP-A) 49-93310, JP-A-49-94619 and JP-A-53-68702, the method of preparing a silver salt of an organic acid in an aqueous solution as disclosed in JP-A-53-31611, JP-A-54-4117 and JP-A-54-46709, the method of preparing a silver salt of an organic acid in an organic solvent as disclosed in JP-A-57-186745, JP-A-47-9432 and U.S. Patent No. 3,700,458 and so forth. Basically, the preparation is carried out by heating an organic acid to a

temperatur higher than its melting point to melt it in water, adding sodium hydroxide or an alkali metal salt with vigorous stirring, and then adding a solution containing silver ions in order to convert the alkali soap into silver soap.

【0006】

Such alkali soap forms micelles in an aqueous solution, and gives a solution of whitely turbid appearance. The reaction from such a micelle state to the silver soap often suffers from problems concerning production stability. Therefore, as a method for obtaining the alkali soap as a uniform solution, a method of using a mixed solution of water and alcohol as the solvent is disclosed in JP-A-55-40607.

【0007】

Further, as shown in name, alkali soap presents alkalinity. Accordingly, the silver soap will be prepared under a high pH condition in the above case. However, addition of a solution containing silver ions into an alkaline solution produces silver oxide as a by-product. Further, it also generates unintended silver nuclei produced by a trace amount of reducing contaminants, which are unavoidable in view of production process and exhibit high reducing property due to the high pH. Such by-products are extremely disadvantageous from the viewpoint that they degrade performance of photothermographic materials, in particular, they cause undesired fog. In this respect, the aforementioned problems are not solved even in the method disclosed in JP-A-55-40607, which aims at obtaining a uniform solution in order to suppress the generation of the by-products.

【0008】

Further, JP-A-9-127643 discloses a method for producing a silver salt by simultaneous addition of measured amounts of an alkali metal salt solution and a silver nitrate solution, and refers to simultaneous addition of a solution of sodium behenate in a mixture of water and isopropyl alcohol and a solution of silver nitrate. This method can at least shift the pH of the reaction from the high pH region to a neutral region, and thus it is a preferred method for reducing the generation amount of silver oxide. However, isopropyl alcohol shows weak reducing property, and this makes the method insufficient as a method for completely solving the problem of fog.

Thus, silver salt of a fatty acid should be carefully prepared. In preparing the silver salt of an organic acid, it is required to eliminate reducible materials as possible and control a grain size and grain shape. However, the conventional methods fail to satisfy these requirements.

【0009】

Many conventional thermally processed image recording materials utilizing silver salt of a fatty acid is prepared by coating a coating solution containing an organic solvent such as toluene, methyl ethyl ketone and methanol, to form a photosensitive layer. Use of an organic solvent as a solvent is unfavorable due to insufficient safety in the production process, bad influence to human bodies, high cost for solvent recovery and others. Additionally, use of an organic solvent is not proper in producing a thermally processed image recording material which aims at preservation of environment.

【0010】

When a water-soluble binder is used, an image-forming layer can be formed by a coating solution containing water as a solvent. This is advantages in environment and cost. However, the binders of the water-soluble polymers have poor compatibility with a silver salt of fatty acid. There provides the problems that a practical coated surface can not be obtained, color tone of silver image formed in developed area is brownish or yellowish which is far from a preferable

black color, the fog level is high. Thus, the prepared materials have poor commercial value.
[0011]

In order to obtain a uniform dispersion practically usable as a coating solution containing a silver salt of a fatty acid, it is necessary to obtain a state that the silver salt of an fatty acid is finely dispersed in a solvent without aggregation. For this reason, it is necessary to develop a method for dispersing the silver salt of a fatty acid as fine grains. Usually used is a method comprising separating the formed hydrophobic grains of silver salt of a fatty acid as solid by filtration, mixing a dispersing agent with the solid, and dispersing the mixture again, as described in *Imaging Processes and Materials, supra*.

[0012]

As the method for dispersing a silver salt of a fatty acid as fine grains, the method of mechanically dispersing it in the presence of a dispersing aid by means of known pulverization mean. However, this method not only produces only a coating solution containing a lot of aggregated particles, and a coating solution that gives bad coated surface quality. Because the method highly possibly grinds primary grains of a silver salt of a fatty salt originally crystallized as a hardly wafer-soluble salt without any selectivity, silver nuclei are formed at crystal cleavage surfaces and causes increase of fog.

[0013]

Then, several methods have been proposed, wherein the primary grains obtained during the reaction of a solution of alkali metal salt and a solution containing silver ions are utilized as they are, not separating the silver salt of a fatty acid as solid and finely dispersing it. For example, JP-A-8-234358 discloses a method of adding silver nitrate to an aqueous dispersion in which fine grains of an alkali salt of a fatty acid are dispersed, and desalting the obtained dispersion of a silver salt of a fatty acid by ultrafiltration. The above reference further refers to enhancement of the dispersion stability by carrying out the ultrafiltration for a dispersion preliminarily containing water-soluble protective colloids such as polyvinyl alcohol and gelatin. However, the shape of the silver salt of a fatty acid obtained by this method is limited to an acicular shape, and in addition, it is difficult to control the grain size in this method. Therefore, it is still insufficient for stably obtaining performance of low fog, high blackening concentration and low haze, which are desired for photothermographic materials.

[0014]

Further, JP-A-9-127643 discloses a method of directly desalting a dispersion of a silver salt of a fatty acid obtained by simultaneous addition of measured amounts of a solution of an alkali metal salt and a silver nitrate solution by means of dialysis or ultrafiltration. By this method, at least the primary grains obtained during the crystallization of the silver salt of a fatty acid can be introduced into a photosensitive layer as they are without degrading the grains. However, problems concerning aggregation of grains under a high salt concentration circumstance, increase of viscosity upon concentration of the dispersion and so forth are not solved, and thus this method is still insufficient as practical means for obtaining a uniform dispersion.

[0015]

[Problems to be resolved by the invention]

In consideration of the problems of the prior arts, the object of the prevent invention is to provide a method of preparing a stable dispersion, that can provide a coated surface of high quality, without isolating a silver salt of an organic acid as a solid and distributing it again. In particular, the object of the present invention is to provide a method in which increase in

viscosity in a concentration process by ultrafiltration and decrease in speed at ultrafiltration are suppressed. Further, the object of the present invention is to provide a thermally processed image recording material exhibiting low fog, high black concentration and low haze, and a method for preparing the material.

【0016】

The inventors conducted extensive study and found that efficient concentration can be conducted with suppressing increase in viscosity in a concentration process by ultrafiltration, decrease in speed at ultrafiltration and blocking of pipeline when dispersion is carried out before or during the concentration process by ultrafiltration, whereby the present invention was provided.

The present invention provides a method for preparing an aqueous dispersion of grains of silver salt of an organic acid that is obtained by dispersing the silver salt grains of the organic acid into an aqueous solvent; which comprises the steps of reacting (1) a solution containing silver ion in water or in a mixture of organic solvent and water with (2) a solution containing an alkali metal salt of the organic acid in water or in a mixture of an organic solvent and water, or in an organic solvent, to obtain a silver salt of the organic acid, and conducting dispersion with a high pressure homogenizer or high speed rotary homomixer in the presence of a dispersing agent, and removing by-product salts by ultrafiltration. The present invention also provides a method for preparing an aqueous dispersion of grains of silver salt of an organic acid that is obtained by dispersing the grains of silver salt of the organic acid into an aqueous solvent; which comprises the steps of reacting (1) a solution containing silver ion in water or in a mixture of organic solvent and water with (2) a solution containing an alkali metal salt of the organic acid in water or in a mixture of an organic solvent and water, or in an organic solvent, to obtain a silver salt of the organic acid, and conducting dispersion with a high pressure homogenizer or high speed rotary homomixer in the presence of a dispersing agent with by-product salts being removed by ultrafiltration.

【0017】

A dispersing agent using in the present invention is preferably having a molecular weight of 3000 or less and anionic surfactant of 8-40 carbon atoms. The concentration of the dispersion is preferably 1-30 weight %, more preferably 3-20 weight % of the dispersoid. The concentration of the grains of silver salt of an organic acid is preferably 1-10 weight % immediately after the above reaction and preferably concentrated by ultrafiltration after the by-product salts are removed by ultrafiltration. After the electric conductivity comes to be 20 $\mu\text{S}/\text{cm}$ or more to less than 300 $\mu\text{S}/\text{cm}$ due to the removal of by-product salts by the ultrafiltration, the dispersion can be preferably concentrated to a concentration of 10-70 weight %, more preferably 20-50 weight %.

【0018】

The present invention further provides a method for producing a thermally processed image recording material comprising a silver salt of an organic acid, a reducing agent for silver ions and a binder on at least one surface of a support, which comprises a step of applying a coating solution for image-forming layer containing an aqueous dispersion of grains of silver salt of an organic acid prepared by any one of the aforementioned preparation methods. The coating solution for image-forming layer preferably contains a photosensitive silver halide and a polymer showing an equilibrated moisture content of 2 weight % or less at 25°C and relative humidity of 60% in the form of latex as the binder, and 30 weight % or more of the solvent of the coating solution preferably consists of water.

It should now be noted that, in this specification, any notation using a word "to" indicates a range defined by values placed before and after such word, where both ends of such range are included as minimum and maximum values.

【0019】

【Detailed description of the preferred embodiment】

Hereafter, it describes a method for preparing an aqueous dispersion of grains of silver salt of an organic acid, a thermally processed image recording material and its method of preparation according to the present invention. In a method of preparing an aqueous dispersion of grains of silver salt of an organic acid, the silver salt of organic acid is prepared by reacting (1) a solution containing silver ion in water or in a mixture of organic solvent and water (hereinafter, it shows "a solution of silver ion") with (2) a solution or suspension containing an alkali metal salt of the organic acid in water or in a mixture of an organic solvent and water, or in an organic solvent (hereinafter, it shows "an alkali metal salt of organic acid").

【0020】

As the ion source for a solution containing silver ion used in the present invention, water-soluble silver salt can be used. As the wafer-soluble silver salt, silver nitrate is preferably used. The concentration of the silver salt in the solution containing silver ions is preferably 0.03-6.5 mol/L, more preferably 0.1-5 mol/L. The pH of the solution containing silver ions is preferably 1-6, more preferably 1.5-4. For the pH adjustment, acids and alkaline usually used for pH adjustment may be added to the solution containing silver ions. As the solvent of the solution containing silver ions used for the present invention, either water or a mixture of water and an organic solvent is used. The organic solvent used for the solution containing silver ions is not particularly limited so long as it is miscible with water. However, those degrading photographic performance are not preferred. While preferred solvents are water-miscible alcohols and acetone, a tertiary alcohol having 4-6 carbon atoms is preferably used. When a tertiary alcohol having 4-6 carbon atoms is used, the tertiary alcohol constitute 70 volume % or less, preferably 50 volume % or less, of the total volume of the solution containing silver ions. Temperature of the solution containing silver ions is preferably 1-60°C, more preferably 5-40°C. When a solution containing silver ions and an aqueous tertiary alcohol solution of organic acid alkali metal salt are simultaneously added as described below, the temperature is most preferably 5-15°C.

【0021】

The organic acid moiety for the alkali metal salt of an organic acid is selected from those stable to light at an ambient temperature as a silver salt, but when its silver salt is heated at 80°C or higher in the presence of a light exposed photocatalyst (e.g., latent images of photosensitive silver halide) and a reducing agent, it produces a silver image. The organic acid is preferably a long chain aliphatic carboxylic acid containing 10-30 carbon atoms, more preferably 12-26 carbon atoms. Preferred examples of the aliphatic carboxylic acid include cerotic acid, lignoceric acid, behenic acid, erucic acid, arachidic acid, stearic acid, oleic acid, lauric acid, caproic acid, myristic acid, palmitic acid, maleic acid, fumaric acid, tartaric acid, linolic acid, butyric acid, camphoric acid and mixtures thereof. More preferred are behenic acid, arachidic acid, stearic acid, oleic acid, lauric acid, caproic acid, myristic acid, palmitic acid, and mixtures thereof.

As the alkali metal moiety for the alkali metal salt of an organic acid, sodium, potassium and so forth can be mentioned. An alkali metal salt of an organic acid can be prepared by adding sodium hydroxide, potassium hydroxide or the like to an organic acid. In this treatment, it is preferable to use the alkali in an amount less than the equivalent of the organic acid to

remain unreacted organic acid. In this case, the amount of the remaining organic acid is preferably 3-5 mole %, more preferably 3-30 mole %, with respect to the total organic acid. Further, it may be prepared by adding an alkali in an amount exceeding the desired amount, and then adding an acid such as nitric acid and sulfuric acid to neutralize excessive alkali substance.

【0022】

The concentration of the alkali metal salt of an organic acid in the solution containing an alkali metal salt of an organic acid used for the present invention is preferably 5-50 weight %, more preferably 7-45 weight %, further preferably 10-40 weight %. The solvent used for the solution containing an alkali metal salt of an organic acid used for the present invention may be any one of water, an organic solvent and a mixture of water and an organic solvent. When a mixture of water and an organic solvent is used, the amount of the organic solvent is preferably 3-70 volume %, more preferably 5-50 volume %, with respect to the volume of water. In this case, since the optimum solvent volume varies depending on the reaction temperature, the optimum amount is desirably determined trial-and-error basis. In the present invention, a mixed solvent of water and a tertiary alcohol having preferably not more than 15 carbon atoms, more preferably not more than 10 carbon atoms, particularly preferably 4 to 6 carbon atoms, is preferably used as the solvent of the solution containing an alkali metal salt of an organic acid for ensuring uniformity of the solution. Tertiary alcohols in which the number of carbon atoms exceeds 6 may not be preferred since their miscibility with water becomes poor. Among the tertiary alcohols having 4 to 6 carbon atoms, most preferred is tert-butanol as its miscibility with water is the highest of all. Alcohols other than such tertiary alcohols may also be unfavorable since they have a reducing property and adversely affect the process of forming the silver salt of an organic acid. The amount of the tertiary alcohols is preferably 3-70 volume %, more preferably 5-50 volume %, with respect to the volume of water. Temperature of the solution containing an alkali metal salt of an organic acid, which is added for the reaction, is preferably maintained at a temperature required for avoiding crystallization or solidification of the alkali metal salt of an organic acid. Specifically, it is preferably 50-90°C, more preferably 60-85°C, most preferably 65-85°C. Further, the temperature is preferably controlled to be a constant temperature within the aforementioned range in order to control the reaction temperature to be constant. For the pH adjustment, acids and alkalines usually used for pH adjustment may be added to the solution containing an alkali metal salt of an organic acid.

【0023】

The solution containing silver ions and the solution containing an alkali metal salt of an organic acid used for the present invention may be added with compounds of the formula (1) described in JP-A-62-65035, water-soluble group-containing N-heterocyclic compounds such as those described in JP-A-62-150240, inorganic peroxides such as those described in JP-A-50-101019, sulfur compounds such as those described in JP-A-51-78319, disulfide compounds such as those described in JP-A-57-643, hydrogen peroxide and so forth.

【0024】

In the present invention, the silver salt of an organic acid is prepared by reacting a solution containing silver ions and a solution containing an alkali metal salt of an organic acid in mixing means. Since sealed mixing means is preferably used as the mixing means, the present invention will be explained by referring to a case utilizing sealed mixing means.

【0025】

A preferred method is a method in which the process contains a period where the solution containing silver ions and the solution containing an alkali metal salt of an organic acid are

simultaneously added to sealed mixing means (simultaneous addition method). According to the simultaneous addition method, mean grain size of the silver salt of an organic acid can be controlled to achieve narrow grain size distribution. In the simultaneous addition method, it is desirable that 10-100 volume %, more preferably 30-100 volume %, particularly preferably 50-100 volume %, of the total volume to be added is simultaneously added. It is preferable to simultaneously add the solution containing silver ions and the solution containing an alkali metal salt of an organic acid in substantially equimolar amounts. In a case where either one is added in advance, it is desirable that the solution containing silver ions is added first. The amount added in advance is preferably from 0-50 volume %, more preferably from 0-25 volume %, of the total amount to be added. Furthermore, a method described in JP-A-9-127643 wherein pH or silver potential of the reaction mixture is controlled during the reaction may be preferably used.

【0026】

Other than the above, there are various approaches as the method for forming organic acid silver salt grains. To obtain organic acid silver salt grains, it is generally preferable to make solubility of the organic acid silver salt in the reaction field small. Further, according to the study of the inventors of the present invention, it has been revealed that the size of the formed organic acid silver salt grains becomes smaller as the addition time of the solution containing silver ions or the solution containing organic acid alkali metal salt becomes longer. In order to obtain organic acid silver salt grains in a desired size, the reaction time must be determined by try and error. Further, in the present invention, the reaction conditions are preferably controlled so that the concentration of the organic acid silver salt grains immediately after the reaction should become 1-10 weight %.

【0027】

The method of adding a solution of silver ion and a solution of an alkali metal salt of an organic acid is not specifically limited. Examples of such methods include adding the solutions onto the surface of the reaction mixture in reaction vessel, adding the solutions in the form of shower, adding the solutions through an outlet introduced into the reaction vessel, adding the solution from a separate room installed in the reaction vessel, adding the solution through a static type mixer installed in pipeline outside a tank, adding the solution to a separate vessel with a stirrer, and adding the solution to a mixer with a stirrer which is filled with reaction mixture and installed in pipeline outside the tank.

In the present invention, a silver salt of an organic acid may be prepared in any applicable reaction vessel batch-wisely or continuously. Agitation in the reaction vessel may be carried out by any means. Agitation means can be selected on the basis of the required characteristics of the grains. Examples of the agitation means include rotary stirrers and emulsification dispersion machines such as those provided with paddles and propellers, dissolvers and rotary homogenizers, static type mixers such as reciprocal motion type stirrers, static type mixers such as static mixers and through other mixers, combinations thereof and so forth.

【0028】

In the sealed mixing means, a solvent (reaction field solution) can be placed beforehand prior to the addition of the solution containing silver ions or the solution containing organic acid alkali metal salt. While wafer is usually used as the solvent placed beforehand, a mixed solution with the organic solvent used for the solution containing silver ions and the solution containing organic acid alkali metal salt may also be used. Temperature of the liquid contained in the sealed mixing means is preferably 5°C to 70°C, more preferably 10°C to 50°C, most preferably

20°C to 45°C, in order to improve performance as a photographic photosensitive material. Throughout the entire process of the reaction, the reaction temperature is preferably controlled to be a constant temperature selected from the above-defined range. As the case may be, however, the reaction temperature may be controlled in some temperature profiles varying within the above-defined range.

【0029】

The temperature difference between the solution containing an alkali metal salt of an organic acid and the liquid in the sealed mixing means is preferably 20°C to 85°C, more preferably 30°C to 80°C. In this case, it is desirable that the temperature of the solution containing an alkali metal salt of an organic acid should be higher than that of the liquid contained in the sealed mixing means. By performing the process as described above, the rate at which the solution containing an alkali metal salt of an organic acid having a higher temperature is rapidly cooled by the reaction vessel and precipitated to give fine crystals, and the rate at which an organic acid silver salt is formed by the reaction with the water-soluble silver salt are both favorably controlled, and thereby the crystal morphology, crystal size and crystal size distribution of the organic acid silver salt can be favorably controlled. In addition, the properties of the thermally processed image recording material, in particular, photothermographic image recording material, can also be improved simultaneously.

【0030】

In order to prepare scaly silver salt of an organic acid preferred for the present invention, for example, when a solution containing silver ions is reacted with a tertiary alcohol aqueous solution containing an alkali metal salt of an organic acid in sealed mixing means (the method includes a step of adding the aqueous tertiary alcohol solution containing an alkali metal salt of an organic acid into a liquid contained in sealed mixing means), the temperature difference between the liquid already existing in the sealed mixing means and the aqueous tertiary alcohol solution of an alkali metal salt of an organic acid to be added thereto is controlled to be between 20°C and 85°C, wherein the liquid in the reaction vessel is a solution containing silver ions put into the reaction vessel in advance, or alternatively, the liquid is water or a mixed solvent of water and a tertiary alcohol in a case where the solution containing silver ions is not put into the reaction vessel in advance but is added from the beginning simultaneously with an aqueous solution of an alkali metal salt of an organic acid in a tertiary alcohol, and when the solution containing silver ions is put into the reaction vessel in advance, water or a mixed solvent of water and a tertiary alcohol may be placed in advance. By maintaining the temperature difference during the addition of the aqueous tertiary alcohol solution containing an alkali metal salt of an organic acid, the crystal morphology of the silver salt of an organic acid or the like can be favorably controlled. The tertiary alcohol may be added in any timing during the preparation of the organic acid silver salt. However, the tertiary alcohol is preferably added at the time of preparation of the organic acid alkali metal salt to dissolve the organic alkali metal salt. The tertiary alcohol may be added in any amount of from 0.01 to 10 as weight ratio based on the weight of water used as a solvent for the preparation of the organic acid silver salt, and preferably added in an amount of from 0.03 to 1.

【0031】

In the preparation methods of the present invention, as for the silver/alkali metal ratio after the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid, it is preferred that the alkali should be excessive by 1-20 mole %, more preferably 1-10 mole %. Further, the concentration of the grains of organic acid silver salt

immediately after the reaction is preferably 1-20 weight %, more preferably 1-10 weight %. The organic acid silver salt grains prepared by the methods of the present invention and used for the preparation of the thermally processed image recording material preferably have a diameter as sphere of 0.1-0.8 micrometers, more preferably 0.1-0.6 micrometers. Further, they preferably have a ratio of long side length/short side length of grains of 1-4, more preferably 1-3, particularly preferably 1-2. Furthermore, the grains preferably have an aspect ratio (grain size for main plane (diameter as circle)/thickness of grain) of 2-30, more preferably 2-15. Further, the grains preferably have a thickness of 0.01-0.20 micrometers, more preferably 0.01-0.15 micrometers. The grains are characterized by containing such grains satisfying the aforementioned requirements in an amount of 30-100%, more preferably 50-100%, particularly preferably 70-100%, in terms of a ratio to the projected area of total grains.

【0032】

The grain size distribution of the silver salt of an organic acid is preferably monodispersed one as far as possible. When a coefficient of variation is defined as a value 100 times as large as a value obtained by dividing the standard deviation of grain size by the grain size, the coefficient of variation is preferably 20% or less, more preferably 18% or less, further preferably 15% or less. As for the measurement method, for example, the grain size (volume weight average diameter) can be determined by irradiating silver salt of an organic acid dispersed in a liquid with a laser ray and determining an autocorrelation function of the fluctuation of the scattered light on the basis of the change in time (the so-called dynamic light scattering method).

【0033】

In a method for preparing an aqueous dispersion of grains of silver salt of an organic acid of the present invention, wherein grains of silver salt of an organic acid are prepared by reacting a solution containing silver ions and a solution containing an alkali metal salt of an organic acid, then dispersion operation is performed by a high pressure homogenizer or high speed rotary homomixer in the presence of a dispersing agent, and by-product salts are removed by ultrafiltration after or during the dispersion operation.

【0034】

In the methods of the present invention, a dispersing agent is preferably added to the system before the start of the reaction of the solution containing silver ions and the solution containing organic acid alkali metal salt or before ultrafiltration. The addition method is not particularly limited. For example, the dispersing agent may be contained in one to three kinds among the solution containing silver ions, the solution containing organic acid alkali metal salt and the solution put into the reaction vessel beforehand. The dispersing agent may also be added separately as a dispersing agent, or added as an additive comprising the dispersing agent and other components. When such a dispersing agent or additive is added, any one of water, organic solvent and mixture of water and an organic solvent may be used as a solvent. These addition methods may be used in any combination.

【0035】

The dispersing agent used in the present invention is preferably an anionic surfactant having a molecular weight of 3000 or less. The molecular weight is preferably 100-3000, more preferably 100-2000. The preferable anionic surfactant having a molecular weight of 3000 or less is an anionic surfactant which is soluble in water or a mixture of water and an organic acid (they may be referred as "aqueous medium"), is capable of dispersing a generated silver salt of an organic acid and has 8-40 carbon atoms, more preferably 12-40. The hydrophilic group may be any anionic group such as carboxylates, sulfuric acid ester salts, sulfonates and phosphoric

acid ester salts. Preferable anionic groups are sulfuric acid ester salts and phosphoric acid ester salts, particularly those having an aromatic group, which impart an excellent dispersion stability under a high ionic strength with by-product salts produced by a reaction of a solution containing silver ion and a solution of alkali metal salt of an organic acid. Examples of the dispersing agents having a molecular weight of 3000 or less include sodium tetradecon-2,3-ene-1-sulfonate (molecular weight 299), sodium diisobutylnaphthalenesulfonate, triisopropylnaphthalenesulfonic acid (molecular weight 357), and naphthalenesulfonic acid oligomer (average molecular weight 1,250), etc.

【0036】

The addition amount of the dispersing agent having a molecular weight of 3000 or less varies on, for example, types and grain size of the surfactant used. The amount of the above dispersing agent is not particularly limited so long as the produced silver salt of an organic acid does not aggregate. The amount is generally 0.1 to 30 weight %, preferably 1 to 30 weight %, more preferably 3 to 20 weight % of the dispersing agent (the silver salt of an organic acid). To attain an absorption rate that is almost the same as the generation rate of the grains of silver salt of an organic acid, the amount of the dispersing agent is preferably 5 to 100 times, more preferably 20 to 80 times larger than the critical micelle concentration. As stated above, it is not specifically limited when the surfactant having a molecular weight of 3000 or less is introduced. Since the hydrophilic alkaline metal salt of an organic acid reacts with silver ion to form a hydrophobic silver salt of the organic acid whereby grains aggregate readily, it is preferable that the surfactant is introduced before completion of the addition of the solution containing silver ion.

【0037】

The dispersing agents having a molecular weight of more than 3000 can be also used. Such a dispersing agent can suitably be selected for use from known polymers, for example, synthetic anionic polymers such as polyacrylic acid, naphthalenesulfonic acid polymers, copolymers of acrylic acid, maleic acid copolymers, maleic acid monoester copolymers and copolymers of acryloylmethylpropane-sulfonic acid; semi-synthetic anionic polymers such as carboxymethyl starch and carboxymethyl cellulose; anionic polymers such as alginic acid and pectic acid; other polymers including polyvinyl alcohol (e.g., PVA-217 (trade name), mean polymerization degree: about 1700), polyvinylpyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxy-propylmethyl cellulose etc., naturally occurring macromolecular compounds such as gelatin and so forth.

【0038】

In the present invention, a nonionic macromolecular dispersing agent is preferably used as a dispersing agent having a molecular weight of 3000 or more. More preferred is a nonionic macromolecular dispersing agent soluble in an aqueous reaction medium, which can disperse a silver salt of an organic acid and has a molecular weight of 5 times to 10 times the fractional molecular weight of an ultrafiltration membrane used for the desalting of the by-product salts produced from the reaction of the solution containing silver ions and the solution containing an alkali metal salt of an organic acid. As such a dispersing agent, polyvinyl alcohol, polyvinylpyrrolidone, hydroxyethyl cellulose and hydroxypropyl cellulose can preferably be used.

The concentration of the dispersing agent having a molecular weight of 3000 or more, preferably nonionic macromolecular dispersing agent is preferably 0.1-30 weight %, particularly preferably 0.5-30 weight %, of the silver salt of an organic acid. While the addition time of the dispersing agent having a molecular weight of 3000 or more, preferably nonionic macromolecular dispersing agent is not particularly limited, it is preferably added after completion of the reaction

of the silver salt of an organic acid and before completion of the ultrafiltration operation in order to prevent inhibition of the reaction of the silver salt of an organic acid.

【0039】

The organic acid silver salt is extremely hydrophobic, and therefore, if the system does not contain a dispersing agent, crosslinking of the grains proceeds with time, and aggregation may remarkably advance by a certain shearing field or pressure field during feeding operation or filtration through an ultrafiltration membrane described later. Further, in a strong ion strength environment before the desalting operation, surface charge of the organic acid silver salt grains is shielded, and hence they may be brought into a condition under which they are further likely to aggregate. In order to ameliorate this condition, it is desirable that pH is selected to be high so that dissociation of the species present on the grain surfaces should be accelerated. However, if the alkalinity in the environment becomes unduly high, the actions of silver oxide or reducing agent as impurity will be increased, and thus they cause fog. Therefore, in order to prevent the aggregation, pH of the dispersion must be maintained to be 6 or higher, preferably 6-8, until the electric conductivity reaches a level less than 2,000 $\mu\text{S}/\text{cm}$ and not less than 500 $\mu\text{S}/\text{cm}$ in the desalting operation by ultrafiltration. Even though a dispersing agent is used, pH of the dispersion is preferably controlled within this range.

【0040】

In the third preparation method of the present invention, the organic acid silver salt is dispersed as fine grains in the presence of a dispersing agent by using pulverization means. Examples of the pulverization means include high-speed mixer, homogenizer, high-speed impact mill, Banbury mixer, homomixer, kneader, ball mill, vibrating ball mill, planetary ball mill, attriter, sand mill, bead mill, colloid mill, jet mill, roller mill, trone mill, high-speed stone mill, high pressure homogenizer, ultrasonic dispersing machine and so forth. In the third preparation method of the present invention, at least high-pressure homogenizer or high-speed rotary type homomixer is used for dispersion.

【0041】

The high-pressure homogenizer is an apparatus for dispersing a dispersion system at a high pressure and high speed, in which large shearing force is applied to the dispersion system. Dispersion is attained with high pressure and high speed in a high pressure grinding section provided in the way of dispersion route, dispersion, emulsification and grinding are attained by passing a dispersion through a narrowed part of dispersion route at high pressure and high speed, or dispersions are collided with each other in a dispersion route.

As for the high-pressure homogenizer, it is generally considered that fine and uniform dispersion can be efficiently achieved therein by enhancing (a) "shear force" to be generated at the passage of a dispersoid through a narrow slit (75 micrometers to 350 micrometers or so) under high pressure at high speed and (b) "cavitation force" to be generated by the pressure releasing, but without changing the preceding impact force resulting from the liquid-liquid collision or the liquid-wall collision in the high-pressure narrow space. One old example of the dispersion apparatus of this type is a Golline homogenizer. In this apparatus, a liquid to be dispersed introduced under high pressure is converted into a high-speed flow when it is passed through a narrow gap formed on the wall of a cylindrical surface. Then, the flow collides against a surrounding wall with its own force, and is emulsified and dispersed by the impact force. For the liquid-liquid collision mentioned above, for example, there can be mentioned a Y-type chamber of Microfluidizer, a spherical chamber utilizing a spherical check valv such as that described in JP-A-8-103642 and so forth. For the liquid-wall collision, there can be mentioned

a Z-type chamber of Microfluidizer and so forth. The pressure is generally 100 to 600 kg/cm², and the flow rate is generally a few meters/sec to 30 meters/sec. In order to increase the dispersion efficiency, some apparatuses are designed wherein the high flow rate area is so modified as to have a serrated configuration, thereby increasing the frequency of collision. Typical examples of such apparatuses are Golline homogenizer (15MR-8TA produced by Golline, produced by APV), High pressure homogenizer (produced by Izumi Food Machinery Co., Ltd.), Microfluidizer produced by Microfluidex International Corporation, Microfluidizer from Mizuh Kogyo Co., Ltd., Nanomizer from Tokushu Kika Kogyo Co., Ltd, Nanomizer LA53 produced by Nanomizer Co., Ltd., Nanomizer produced by Cosmo Keiso Co., Ltd, high pressure homogenizer such as Genus PY produced by Genus Co., Ltd. and so forth. Other examples of such apparatuses are described in JP-A-8-238848, JP-A-8-103642 and U.S. Patent No. 4,533,254.

In dispersing process of the organic acid silver salt, dispersion having a desired grain size may be obtained by controlling the flow rate, the difference in the pressure before and after at the pressure releasing and the frequency of the processing. The flow rate is preferably from 100 to 600 m/sec and the difference in pressure at the pressure releasing is preferably from 200 to 3,000 kg/cm².

【0042】

Examples of high speed rotary type homomixer include high-speed shearing mix r produced by Tokushu Kika Kogyo Co., Ltd. (trade name: TK Homomixer), Milder MDN 303V produced by Ebara Corp. and so forth. While the rotation number may vary depending on capacity of dispersing machine, size of impellers and so forth, it is preferably about 1000-30000 rpm.

It is not preferable to expose such an aqueous dispersion to a high temperature under a high pressure in view of dispersibility and photographic performance. At a high temperature above 90°C, a grain size may readily become large and fog may be increased. Accordingly, the water dispersion is preferably kept at a temperature of from 5°C to 90°C, more preferably from 5°C to 80°C, particularly preferably from 5°C to 65°C, by a cooling step using a cooling apparatus during or after the dispersion in a high-pressure homogenizer or high-pressure rotary homomixer. The cooling apparatus may be appropriately selected from a double pipe or triple pipe with a static mixer, a multi-tubular heat exchanger, a coiled heat exchanger and so forth depending on an amount of heat exchange to be required. The size, wall thickness or material of pipes may be appropriately selected to increase heat exchange efficiency depending on an applied pressure. In addition, depending on an amount of heat exchange, a refrigerant used in the cooling apparatus may be a well water at 20°C or a chilled water at from 5 to 10°C cooled by a refrigerator, and if desired, a refrigerant such as ethylene glycol/water at -30°C may also be used.

【0043】

Further, in the third preparation method of the present invention, ultrafiltration is performed after or during the aforementioned dispersion operation. As the method for ultrafiltration performed in the present invention, methods used for desalting and concentration of silver halide emulsion, and for example, those methods described in Research Disclosure, No. 10208 (1972), No. 13122 (1975), No. 16351 (1977) etc. can be used. While pressure difference and flow rate, which are important as the operational conditions, can be selected by referring to the characteristic curves mentioned in Haruhiko Oya, "Maku Riyo Gijutsu Handbook (Membrane Utilization Technique Handbook)", published by Saiwai Shobo (1978), p.275, it is necessary to find out optimum conditions for treating an organic acid silver salt dispersion of interest in order to suppress aggregation of grains, fog and so forth. As an ultrafiltration membrane, modules of

plate type, spiral type, cylinder type, hollow yarn type, hollow fiber type and so forth, in which a membrane is already incorporated, are commercially available from Asahi Chemical Industry Co., Ltd., Daicel Chemical Industries, Ltd., Toray Industries, Inc., NITTO DENKO CORP. and so forth. In view of the total membrane are, washability and so forth, those of hollow yarn type and spiral type are preferred. Examples of the material of ultrafiltration membrane include polysulphone, polyphenyl sulphone, polyether sulphone, polyacrylonitrile and so forth, and examples of module type include flat membrane, hollow yarn membrane, tubular membrane and so forth. The fractional molecular weight, which is an index of a threshold for substances that can permeate a membrane, must be determined based on the molecular weight of the used dispersing agent. In the present invention, those having a fractional molecular weight of 1,500–50,000, more preferably 4,000–50,000, are preferably used.

【0044】

In the present invention, it is preferable to perform the desalting treatment after the organic acid silver salt grains immediately after the reaction is concentrated to a concentration of 15–40 weight %, preferably 15–25 weight %. Further, the liquid temperature after the grain formation is preferably kept low until the desalting operation proceeds. This is because silver nuclei are likely to be formed by the shearing force field and the pressure field during the feeding of dispersion or passage through an ultrafiltration membrane under a condition that the solvent used for dissolving the alkali metal salt of an organic acid permeates in the produced organic acid silver salt grains. For this reason, in the present invention, the ultrafiltration operation is desirably performed while the temperature of the organic acid silver salt grain dispersion is kept at 1–30°C, preferably at 5–25°C.

【0045】

As a method for supplementing the solvent lost due to passage through the membrane, there may be employed either the constant volume method where the solvent is continuously supplemented, or the batch method where the solvent is intermittently added. The constant volume method is preferred in the present invention because of its relatively shorter desalting treatment time. The solvent to be supplemented as described above comprises pure water obtained by ion exchange or distillation, which may contain a pH modifier. However, if the desalting operation is performed by dilution with pure water during the ultrafiltration operation, the concentration of the dispersing agent is reduced and hence aggregation may be caused. Therefore, a surfactant is preferably supplemented in order to maintain a certain level of surfactant concentration to prevent the aggregation. In particular, because the organic acid silver salt grains are in a state that they are likely to aggregate in the high salt concentration circumstance of the early stage of the desalting operation with the presence of an organic solvent such as tertiary alcohol, the concentration of anionic surfactant, for example, is preferably maintained at a level 5 to 100 times as high as the critical micelle concentration. Specifically, while the concentration of leaking surfactant is quantified by spectrophotometry or liquid chromatography, a solution having the same concentration as the measured concentration may be continuously added as a replenisher, or a solution having a concentration higher than that may be added intermittently.

【0046】

Further, since the silver salt of an organic acid is extremely hydrophobic, aggregation may markedly proceed under a shearing field or pressure field during the feeding operation and passage through an ultrafiltration membrane. Furthermore, in a high ionic strength circumstance in early stages of the desalting operation, the surface charge of the organic acid

silver salt grains is shielded, and hence they become more likely to aggregate. In order to ameliorate this condition, when an anionic surfactant is added in advance, another ionic surfactant having anionic nature and a hydrophobic group with 8-40 carbon atoms different from the anionic surfactant added beforehand may be added during the desalting operation. As for the addition method, while the concentration of leaking surfactant is quantified by spectrophotometry or liquid chromatography, a solution having the same concentration as the measured concentration may be continuously added, or a solution having a concentration higher than that may be added intermittently, as described above.

【0047】

If the fractional molecular weight of an ultrafiltration membrane is unknown, its rejection can be obtained by filtering a solution of a dispersing agent to be used, and calculating the rejection from the concentration of the surfactant leaked into the filtrate. When a surfactant is used, the rejection R of an ultrafiltration membrane is defined by the following equation:

$$R = (C_i - C_o)/C_i \times 100 [\%]$$

wherein C_i represent a concentration in original dispersion, and C_o represents a leaked concentration in the filtrate. The rejection is preferably less than 50% for the methods of the present invention.

【0048】

In a preferred embodiment, a dispersing agent having a molecular weight of more than 3,000, preferably a nonionic macromolecular dispersing agent may be added after the desalting is performed by ultrafiltration and thus electric conductivity of the organic acid silver salt dispersion is lowered, but before completion of the desalting operation. At this time, the conductivity is preferably 2000 $\mu\text{S}/\text{cm}$ or less. In this case, in order to remove anionic surfactant having a molecular weight of 3,000 or less and replace it with a dispersing agent having a molecular weight of more than 3,000, preferably a nonionic macromolecular dispersing agent, there is preferably performed an operation of adding pure water in an amount corresponding to the amount of the anionic surfactant solution passed through the ultrafiltration membrane, i.e., the so-called constant volume dilution, in an order of 2- to 20-fold.

【0049】

In the present invention, it is also possible to carry out the ultrafiltration operation while adding a poor solvent for the dispersing agent used after the conductivity has reached a level below 1,000 $\mu\text{S}/\text{cm}$ with the progress of the desalting. Under a low ionic strength circumstance, aggregation is not caused even if the protective effect of the dispersing agent is reduced, because stabilizing effect is exerted by electric charge on the grain surfaces. In addition, the viscosity of the whole dispersion becomes high due to increase of repulsion between the grains, and therefore the filtration operation becomes difficult. In order to avoid this phenomenon, it is desirable to add the poor solvent for the dispersing agent.

【0050】

After the removal of by-product salts by ultrafiltration, the dispersion can be further concentrated by ultrafiltration. In particular, after the electric conductivity comes to be 20 $\mu\text{S}/\text{cm}$ or more to less than 300 $\mu\text{S}/\text{cm}$ due to the removal of by-product salts by the ultrafiltration, the dispersion can be preferably concentrated to a concentration of 10-70 weight %, more preferably 20-50 weight %.

【0051】

In the present invention, metal ions selected from Ca, Mg, Ce, Al, Zn and Ba are preferably added in the form of a water-soluble metal salt, which is not a halide compound.

Specifically, they are preferably added in the form of nitrate or sulfate. Time of the addition of the metal ions selected from Ca, Mg, Ce, Al, Zn and Ba is not particularly limited, and they may be added any time. For example, they may be added to a liquid of organic acid silver salt preparation, preliminarily added to a reaction mixture, added during or immediately after the formation of the organic acid silver salt, or immediately before the coating, i.e., before or after the formation of coating solution. The amount is preferably 10^{-3} to 10^{-1} mole, particularly preferably 5×10^{-3} to 5×10^{-2} mole, per one mole of the organic acid silver salt.

[0052]

When a photosensitive silver halide salt coexists at the time of finely dispersing the silver salt of an organic acid by converting the dispersion into a high-speed flow under a high pressure, fog may increase and sensitivity may markedly decrease. The amount of photosensitive silver halide salt in an aqueous dispersion is 0.1 mole % less per 1 mole of silver salt of organic acid. It is desirable that a photosensitive silver halide salt is not added positively.

[0053]

The prepared dispersion can be stored with stirring to prevent precipitation of the grains during storage, or stored in a highly viscous state formed by means of hydrophilic colloids (e.g., a jelly state formed with gelatin). Furthermore, the dispersion may contain a preservative in order to prevent proliferation of microorganisms during storage. The silver salt of an organic acid solid fine grain dispersion used in the present invention comprises at least a silver salt of an organic acid and water. While the ratio of the silver salt of an organic acid to water is not particularly limited, it must be decided based on rheological characteristics for stable coating and production speed determined by dry moisture content in view of efficient formation of coated films. The silver salt of an organic acid preferably accounts for from 10-70 weight %, particularly preferably from 20-50 weight % of the entire dispersion.

[0054]

The dispersion of organic acid silver salt grains prepared by the preparation methods of the present invention is preferably finely dispersed in an aqueous solvent, and then mixed with an aqueous solution of a photosensitive silver halide salt to provide a coating solution for photosensitive image-forming layer of a photothermographic material. Such a coating solution enables the manufacture of a thermally processed image recording material exhibiting low haze and low fog, and showing high sensitivity. When a photosensitive silver halide salt coexists at the time of finely dispersing the silver salt of an organic acid by converting the dispersion into a high-speed flow under a high pressure, fog may increase and sensitivity may markedly decrease. Therefore, the aqueous dispersion that is dispersed by converting it into a high-speed flow under high pressure preferably contains substantially no photosensitive silver halide salt. Furthermore, when an organic solvent is used as a dispersion medium instead of water, haze and fog may increase and sensitivity may be likely to decrease. On the other hand, when the conversion method where a part of the silver salt of an organic acid in the dispersion is converted into a photosensitive silver halide salt is used instead of the method of mixing an aqueous photosensitive silver halide salt solution, sensitivity may be decreased.

[0055]

The shape of the silver salt of an organic acid that can be used for a thermally processed image recording material, in particular, photothermographic material, is not particularly limited, and scaly grains, acicular grains, rod-like grains and tabular grains can be mentioned. However, scaly silver salt of an organic acid is preferred. Scaly silver salt of an organic acids are herein defined as follows. A sample of a silver salt of an organic acid to be analyzed is

observed with an electronic microscope, and grains of the salt seen in the field are approximated to rectangular parallelepipeds. The three different edges of each rectangular parallelepiped are represented as a, b and c where a is the shortest, c is the longest, and c and b may be the same. From the shorter edges a and b, x is obtained according to the following equation:

$$x = b/a$$

The values of x are obtained for about 200 grains, and an average of them (x (average)) is obtained. Samples that satisfy the requirement of x (average) ≥ 1.5 are defined to be scaly. Scaly grains preferably satisfy $30 \geq x$ (average) ≥ 1.5 , more preferably $20 \geq x$ (average) ≥ 2.0 . In this connection, acicular (needle-like) grains falls satisfy $1 \leq x$ (average) < 1.5 .

【0056】

In scaly grains, it is understood that a corresponds to the thickness of tabular grains of which main planes are defined by the sides of b and c. The average of a is preferably from 0.01 to 0.23 micrometers, more preferably from 0.1 to 0.20 micrometers. The average of c/b is preferably from 1 to 6, more preferably from 1.05 to 4, even more preferably from 1.1 to 3, particularly preferably from 1.1 to 2.

【0057】

The organic acid silver salt grains prepared by the methods of the present invention and used for the preparation of the thermally processed image recording material preferably have a diameter as sphere of 0.1–0.8 micrometers, more preferably 0.1–0.6 micrometers. Further, they preferably have a ratio of long side length/short side length of grains of 1–4, more preferably 1–3, particularly preferably 1–2. Furthermore, the grains preferably have an aspect ratio (grain size for main plane (diameter as circle)/thickness of grain) of 2–30, more preferably 2–15. Further, the grains preferably have a thickness of is 0.01–0.20 micrometers, more preferably 0.01–0.15 micrometers. The grains are characterized by containing such grains satisfying the aforementioned requirements in an amount of 30–100%, more preferably 50–100%, particularly preferably 70–100%, in terms of a ratio to the projected area of total grains.

【0058】

The grain size distribution of the silver salt of an organic acid is preferably monodispersed one as far as possible. When a coefficient of variation is defined as a value 100 times as large as a value obtained by dividing the standard deviation of grain size by the grain size, the coefficient of variation is preferably 20% or less, more preferably 18% or less, further preferably 15% or less. As for the measurement method, for example, the grain size (volume weight average diameter) can be determined by irradiating silver salt of an organic acid dispersed in a liquid with a laser ray and determining an autocorrelation function of the fluctuation of the scattered light on the basis of the change in time (the so-called dynamic light scattering method).

【0059】

The grain size (volume weight average diameter) in an organic acid silver salt solid dispersion can be obtained form a grain size (volume weight average diameter) determined by, for example, irradiating silver salt of an organic acid dispersed in a liquid with a laser ray and determining an autocorrelation function of the fluctuation of the scattered light on the basis of the change in time. Preferred is a solid fine grain dispersion having a mean grain size of 0.05 to 10.0 micrometers, more preferably from 0.1 to 5.0 micrometers, further preferably from 0.1 to 2.0 micrometers.

【0060】

The mixing ratio of the photosensitive silver halogenate to the silver salt of an organic acid can be determined based on the purpose of the thermally processed image recording material.

The ratio is preferably 1 to 30 mole %, more preferably 3 to 20 mole %, particularly preferably 5 to 15 mole %. In order to control the photographic properties, it is preferable to mix two or more aqueous dispersions of a silver salt of an organic acid with two or more aqueous dispersions of photoinsensitive silver halide.

The silver salt of an organic acid may be used in any desired amount in the thermally processed image recording material. However, it is preferably used in an amount of 0.1-5 g/m², more preferably 1-3 g/m², in terms of silver amount.

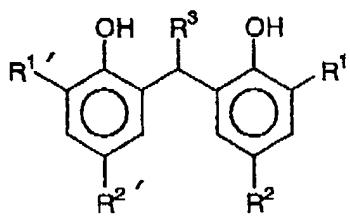
【0061】

The thermally processed image recording material utilizing the organic acid silver salt grains prepared by the methods of the present invention preferably contains a reducing agent for the organic acid silver salt. The reducing agent for the organic acid silver salt may be any substance (preferably, organic substance) capable of reducing silver ions into silver. Some examples of the reducing agent are described in JP-A-11-65021, paragraphs 0043 to 0045, EP 0803764A1, from page 7, line 34 to page 18, line 12, Japanese Patent Application Nos. 2000-16661, 2000-208 and 2000-2428.

Especially preferred are bisphenol-type reducing agents, and preferred examples thereof are mentioned below, but not limited to these.

【0062】

【Chemical formula 1】



	R ¹	R ¹ '	R ²	R ² '	R ³
I-1	CH ₃	CH ₃	CH ₃	CH ₃	H
I-2	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
I-3	CH ₃	CH ₃	CH ₃	CH ₃	C ₃ H ₇
I-4	CH ₃	CH ₃	CH ₃	CH ₃	i-C ₃ H ₇
I-5	CH ₃	CH ₃	CH ₃	CH ₃	CH(C ₂ H ₅)C ₄ H ₉
I-6	CH ₃	CH ₃	CH ₃	CH ₃	CH ₂ CH(CH ₃)CH ₂ C(CH ₃) ₃
I-7	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅	H
I-8	CH ₃	CH ₃	C ₂ H ₅	C ₂ H ₅	i-C ₃ H ₇
I-9	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₃	H
I-10	C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₃	i-C ₃ H ₇
I-11	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	H
I-12	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃
I-13	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	C ₂ H ₅
I-14	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₃ H ₇
I-15	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₄ H ₉
I-16	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₇ H ₁₅
I-17	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₁₁ H ₂₃
I-18	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	i-C ₃ H ₇
I-19	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH(C ₂ H ₅)C ₄ H ₉
I-20	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH(CH ₃) ₂

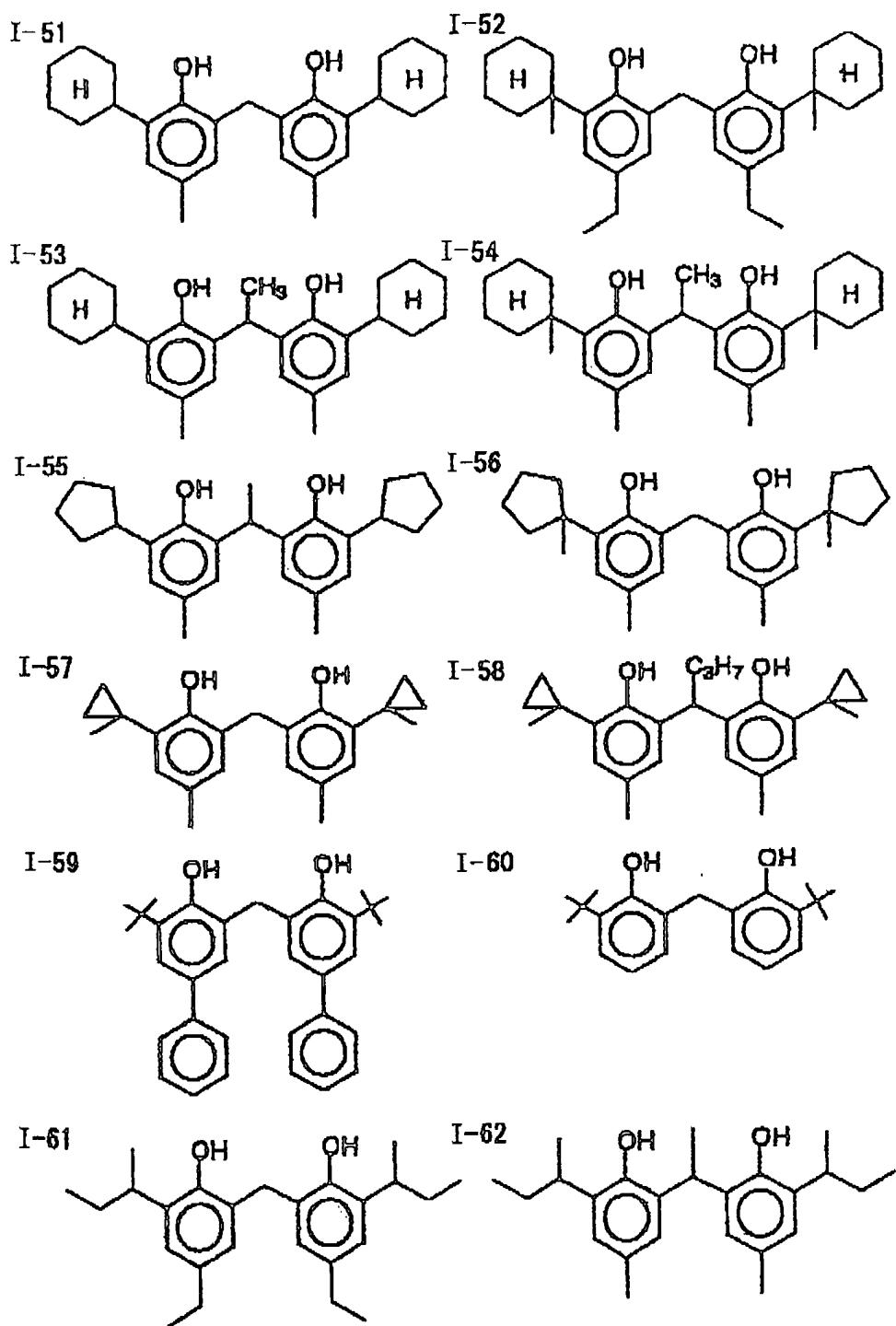
【0063】

【Chemical formula 2】

	R ¹	R ^{1'}	R ²	R ^{2'}	R ³
I-21	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH(CH ₃)CH ₂ C(CH ₃) ₃
I-22	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ OCH ₃
I-23	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH ₂ OCH ₃
I-24	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH ₂ OC ₄ H ₉
I-25	t-C ₄ H ₉	t-C ₄ H ₉	CH ₃	CH ₃	CH ₂ CH ₂ SC ₁₂ H ₂₅
I-26	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	H
I-27	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	CH ₃
I-28	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	n-C ₃ H ₇
I-29	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	i-C ₃ H ₇
I-30	t-C ₄ H ₉	t-C ₄ H ₉	C ₂ H ₅	C ₂ H ₅	CH ₂ CH ₂ OCH ₃
I-31	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₃ H ₇	n-C ₃ H ₇	H
I-32	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₃ H ₇	n-C ₃ H ₇	CH ₃
I-33	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₃ H ₇	n-C ₃ H ₇	n-C ₃ H ₇
I-34	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉	H
I-35	t-C ₄ H ₉	t-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉	CH ₃
I-36	t-C ₅ H ₁₁	t-C ₅ H ₁₁	CH ₃	CH ₃	H
I-37	t-C ₅ H ₁₁	t-C ₅ H ₁₁	CH ₃	CH ₃	CH ₃
I-38	t-C ₅ H ₁₁	t-C ₅ H ₁₁	C ₂ H ₅	C ₂ H ₅	H
I-39	t-C ₅ H ₁₁	t-C ₅ H ₁₁	C ₂ H ₅	C ₂ H ₅	CH ₃
I-40	i-C ₃ H ₇	i-C ₃ H ₇	CH ₃	CH ₃	H
I-41	i-C ₃ H ₇	i-C ₃ H ₇	CH ₃	CH ₃	n-C ₃ H ₇
I-42	i-C ₃ H ₇	i-C ₃ H ₇	C ₂ H ₅	C ₂ H ₅	H
I-43	i-C ₃ H ₇	i-C ₃ H ₇	C ₂ H ₅	C ₂ H ₅	n-C ₃ H ₇
I-44	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	H
I-45	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	CH ₃
I-46	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃	H
I-47	t-C ₄ H ₉	CH ₃	CH ₃	n-C ₃ H ₇	CH ₃
I-48	t-C ₄ H ₉	CH ₃	CH ₃	CH ₃	n-C ₃ H ₇
I-49	t-C ₄ H ₉	CH ₃	t-C ₄ H ₉	CH ₃	CH ₃
I-50	i-C ₃ H ₇	CH ₃	CH ₃	CH ₃	CH ₃

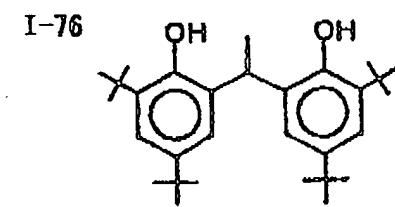
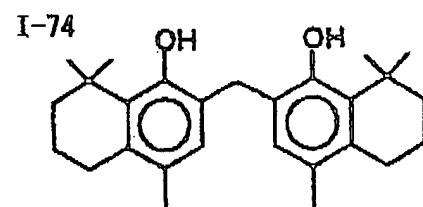
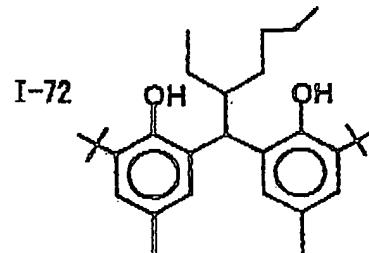
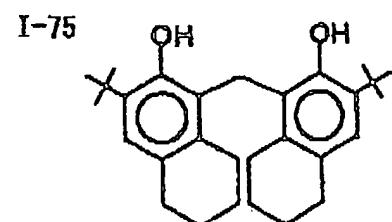
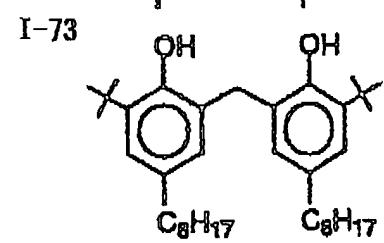
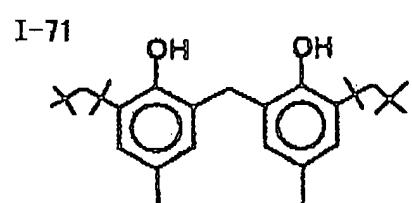
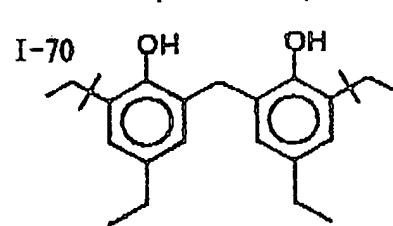
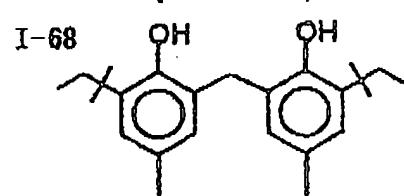
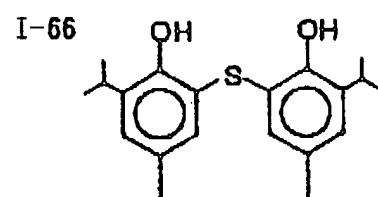
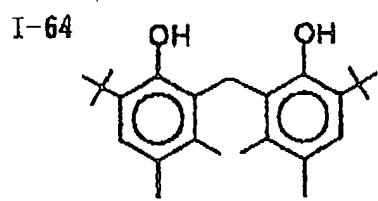
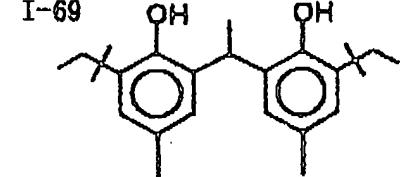
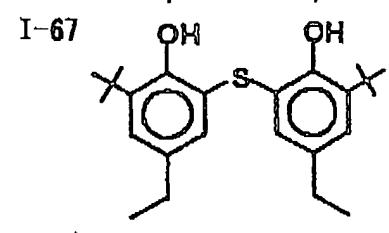
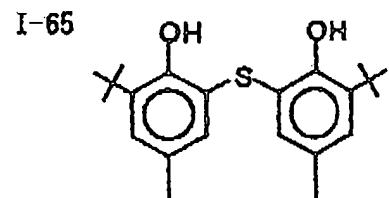
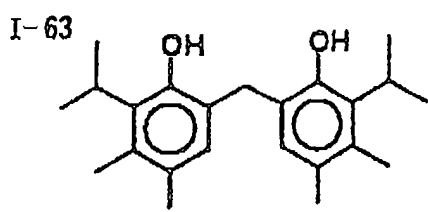
【0064】

【Chemical formula 3】



【0065】

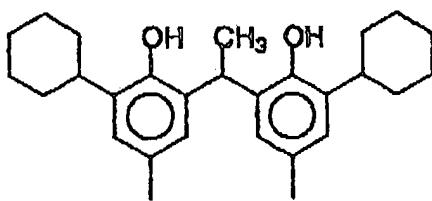
【Chemical formula 4】



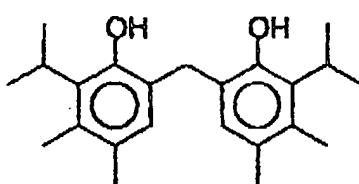
【0066】

【Chemical formula 5】

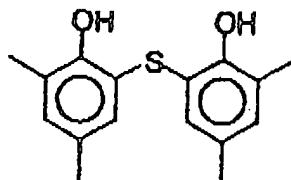
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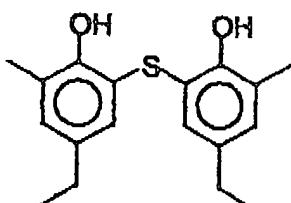
78



79



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【0067】

The amount of the reducing agent is preferably 0.01–5.0 g/m², more preferably 0.1–3.0 g/m². The amount of the reducing agent is preferably 5–50 mole %, more preferably 10–40 mole %, per mole of silver on the image-forming layer side. The reducing agent is preferably contained in the image-forming layer. The reducing agent may be added to a coating solution in any form such as solution, emulsion dispersion and solid microparticle dispersion, so as to be contained in the thermally processed image recording material. As a well known emulsion dispersion method, there can be mentioned a method for mechanically preparing an emulsion dispersion by using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate or diethyl phthalate, ethyl acetate or cyclohexanone as an auxiliary solvent for dissolution.

【0068】

Further, as a method for solid microparticle dispersion, there can be mentioned method for preparing solid microparticle dispersion by dispersing powder of the reducing agent in a suitable solvent such as water using a ball mill, colloid mill, vibration ball mill, sand mill, jet mill and roller mill, or by means of ultrasonic wave. In this operation, protective colloid (e.g., polyvinyl alcohol), surfactant (e.g., anionic surfactants such as sodium triisopropylnaphthalenesulfonate (mixture of those having three isopropyl groups on different positions)) and so forth may be used. An aqueous dispersion may contain a preservative (e.g.,

benzisothiazolinone sodium salt).

【0069】

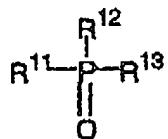
In the thermally processed image recording material, the phenol derivatives represented by the formula (A) mentioned in Japanese Patent Application No. 11-73951 are preferably used as a development accelerator.

【0070】

When the reducing agent has an aromatic hydroxyl group (-OH), in particular when the reducing agent is any of the aforementioned bisphenols, it is preferable to use together a non-reducing compound having a group that can form a hydrogen bond with the aromatic hydroxyl group. Examples of the group that can form a hydrogen bond with hydroxyl group or amino group include phosphoryl group, sulfoxido group, sulfonyl group, carbonyl group, amido group, an ester group, urethane group, ureido group, a tertiary amino group, a nitrogen-containing aromatic group and so forth. Particularly preferred examples of such a compound are those compounds having phosphoryl group, sulfoxido group, amido group (provided that it does not have >N-H group, but it is blocked like >N-R (R is a substituent other than H)), urethane group (provided that it does not have >N-H group, but it is blocked like >N-R (R is a substituent other than H)), or ureido group (provided that it does not have >N-H group, but it is blocked like >N-R (R is a substituent other than H)). Particularly preferred hydrogen bond-forming compounds are compounds represented by the following formula (II).

【0071】

【Chemical formula 6】



【0072】

In the formula (II), R¹², R¹² and R¹³ each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group or a heterocyclic group, and these groups may or may not have one or more substituents. Two of R¹¹, R¹² and R¹³ may be bonded together to form a ring.

When R¹¹, R¹² and R¹³ have one or more substituents, they can be selected from a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamide group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group and so forth, and they are preferably selected from an alkyl group and an aryl group. Specific examples thereof are methyl group, ethyl group, isopropyl group, t-butyl group, t-octyl group, phenyl group, 4-alkoxyphenyl group, 4-acyloxyphenyl group and so forth.

【0073】

Specific examples of the groups represented by R¹¹, R¹² and R¹³ include a substituted or unsubstituted alkyl group such as methyl group, ethyl group, butyl group, octyl group, dodecyl group, isopropyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, phenethyl group and 2-phenoxypropyl group; a substituted or unsubstituted aryl group such as phenyl group, cresyl group, xylyl group, naphthyl

group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-anisidyl group and 3,5-dichlorophenyl group; a substituted or unsubstituted alkoxy group such as methoxy group, ethoxy group, butoxy group, octyloxy group, 2-ethylhexyloxy group, 3,5,5-trimethylhexyloxy group, dodecyloxy group, cyclohexyloxy group, 4-methylcyclohexyloxy group and benzyloxy group; a substituted or unsubstituted aryloxy group such as phenoxy group, cresyloxy group, isopropylphenoxy group, 4-t-butylphenoxy group, naphthoxy group and biphenyloxy group; a substituted or unsubstituted amino group such as amino group, dimethylamino group, diethylamino group, dibutylamino group, dioctylamino group, N-methyl-N-hexylamino group, dicyclohexylamino group, diphenylamino group and N-methyl-N-phenylamino group; a heterocyclic group such as 2-pyridyl group, 4-pyridyl group, 2-furanyl group, 4-piperidinyl group, 8-quinolyl group and 5-quinolyl group, and so forth.

【0074】

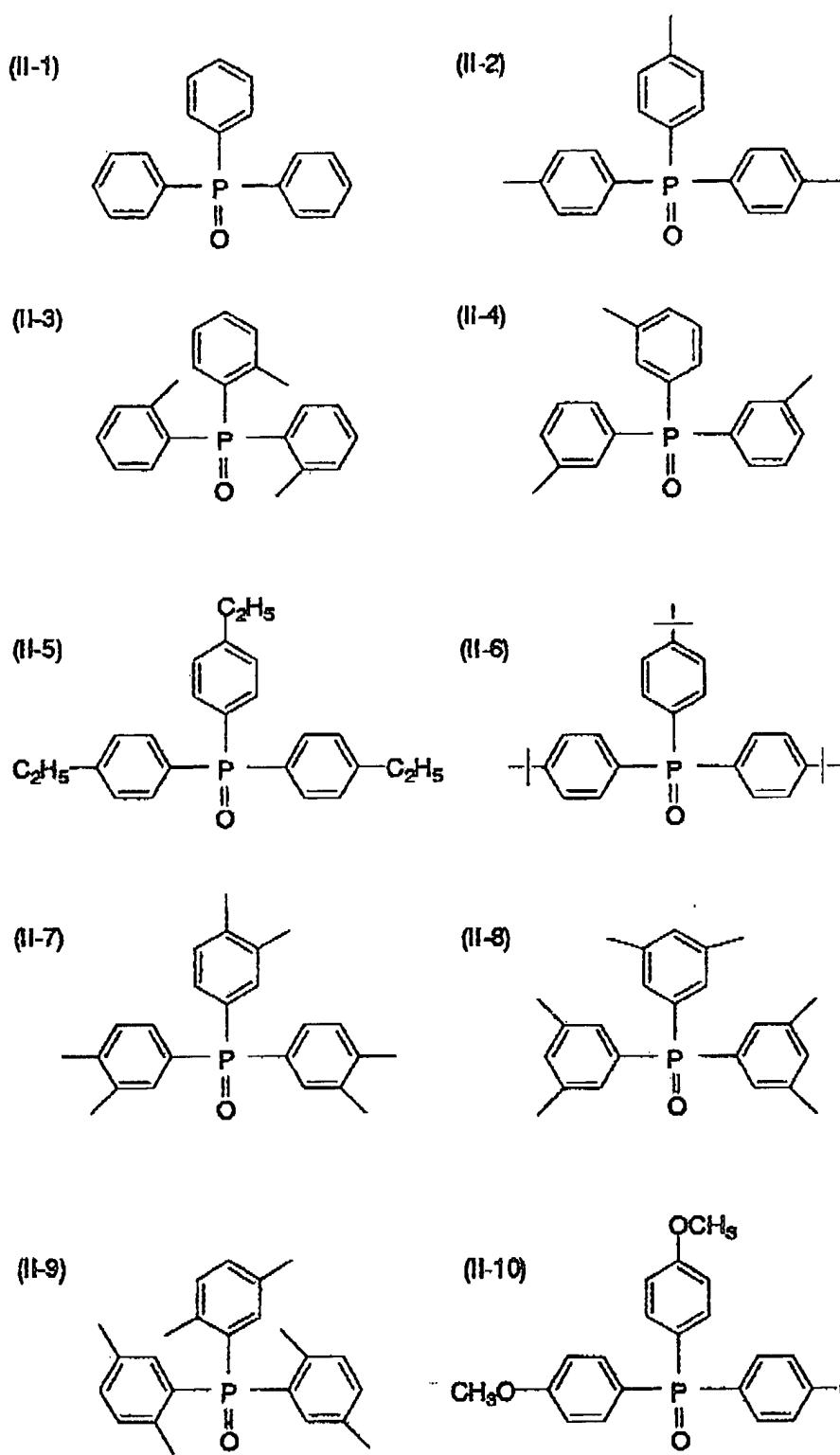
R^{11} , R^{12} and R^{13} are preferably selected from an alkyl group, an aryl group, an alkoxy group and an aryloxy group. It is preferred that one or more of R^{11} , R^{12} and R^{13} should be selected from an alkyl group and an aryl group, and it is more preferred that two or more of R^{11} , R^{12} and R^{13} should be selected from an alkyl group and an aryl group. In view of availability at low cost, it is preferred that R^{11} , R^{12} and R^{13} should be the same groups.

【0075】

Specific examples of the compound represented by the formula (II) will be shown below. However, the compounds that can be used for the present invention are not limited to these examples.

【0076】

【Chemical formula 7】



【0077】
【Chemical formula 8】